

Appendix C

Parametric Variation of the Mass Transfer Coefficient

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A priori specification of the mass transfer coefficient for residual NAPL in the field is difficult as very little field data exist (Zheng et al., 2010; Mobile et al., 2015; Mobile et al., 2016). Decades of research are available from column studies (Mayer & Miller, 1996; DiFilippo et al., 2010). Column studies do not capture soil heterogeneity influencing flow paths around NAPL accumulations or the heterogeneity in the distribution of NAPL in such soils. In addition, most of the research has focused on a single component NAPL as compared to the multi-component NAPL considered here. As a result, most models including complex numerical models assume local equilibrium between NAPL and groundwater, i.e., if a discretized node contains NAPL the water in the node is assumed to be at the equilibrium concentration. This approach is only valid when groundwater velocities are relatively slow and node volumes are relatively small. However, the TEE Pilot Test included a mass transfer testing at ST012 (Kavanaugh et al., 2011, ESTCP Project ER-20083). Subsequent evaluation of the data led to published values for the mass transfer coefficient ranging from 0.022 to 0.6 d⁻¹ (Mobile et al., 2016). The relatively large range reflects the high degree of heterogeneity at the site. A baseline value of 0.05 d⁻¹ is assumed for the conditions of the mass transfer test.

To adjust the parameter for different aquifer conditions and to assess differing remedial processes and strategies, a method is required to modify the baseline NAPL mass transfer coefficient for changes in velocity (i.e., pumping rates), increases in temperature, and reductions in NAPL saturation from extraction or dissolution. To make these adjustments, a parametric form of the dissolution rate constant is employed as suggested by Clement et al. (2004),

$$k_{N,i} = k_{N,i}^0 \left(\frac{S_N}{S_N^0} \right)^{0.75} \left(\frac{D_i}{D_i^0} \right) \left(\frac{Re}{Re^0} \right)^{0.598}, \quad Re = \frac{U \rho_w d_{50}}{\mu_w}$$

where,

$$\begin{aligned} k_{N,i} &= \text{NAPL mass transfer coefficient} \\ S_N &= \text{average NAPL saturation} \\ D_i &= \text{aqueous diffusion coefficient of NAPL component } i \\ Re &= \text{Reynolds Number} \\ U &= \text{Darcy velocity} \\ {}^0 &= \text{superscript designating the base case} \end{aligned}$$

This relationship is based on the many column tests performed in studying single component NAPL dissolution (Mayer & Miller, 1996) with both homogeneous and heterogeneous NAPL

distributions. This expression can account for changes in temperature by adjusting the properties (diffusion coefficient, viscosity, water density). The solubility of NAPL components are similarly adjusted for the change in temperature. Substituting the Reynolds number,

$$k_{N,i} = k_{N,i}^0 \left(\frac{S_N}{S_N^0} \right)^{0.75} \left(\frac{D_i}{D_i^0} \right) \left(\frac{\rho_w \mu_w^0}{\mu_w \rho_w^0} \right)^{0.598} \left(\frac{U}{U^0} \right)^{0.598}$$

Consider next the velocity in terms of a pore volume exchange rate designated by q ,

$$q = \frac{Q}{\phi V_S}$$

$$\begin{aligned} Q &= \text{total groundwater flow rate through } V_S \\ V_S &= \text{volume of NAPL - impacted soil} \\ \phi &= \text{total soil porosity} \end{aligned}$$

Substituting this expression into the parametric relationship for the velocity and noting the porosity is a constant yields,

$$k_{N,i} = k_{N,i}^0 \left(\frac{S_N}{S_N^0} \right)^{0.75} \left(\frac{D_i}{D_i^0} \right) \left(\frac{\rho_w \mu_w^0}{\mu_w \rho_w^0} \right)^{0.598} \left(\frac{q}{q^0} \right)^{0.598}$$

For the mass transfer test described in Mobile et al. (2016), the total flow and estimated NAPL mass are found in the TEE Pilot Test Evaluation Report (BEM, 2011) in Table L.2.4.3.

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The flow rate (Q) through the NAPL-impacted soil volume of each zone is readily specified. The flow was calculated for ambient groundwater conditions and presented in Table 1. Flow for a specific remedial alternative is a basic design parameter and straightforward to estimate. An increased or decreased flow rate also has an auxiliary relationship with the NAPL mass transfer coefficient as discussed below. Values of q presented in Table 5 suggest, under ambient conditions, the saturated pore volumes of the UWBZ and LSZ are flushed roughly every 15 and 25 years allowing a long residence time for material entering the volume (e.g., terminal electron acceptors).

Table C-1. NAPL Mass Transfer Parameters at Ambient Temperature from the Mass Transfer Test (MTT) and Estimated Conditions for EBR

Parameter		LSZ-MTT	LSZ-EBR
M_{NAPL}	(gal)	71,672	54,821
V_{Soil}	(yd ³)	18,730	38,500
S_{NAPL}	(-)	0.058	0.024
Q	(gpm)	35	3.5
q	(1/day)	0.038	0.00185
$k_{\text{N,benzene}}$	(1/day)	0.05	0.0042